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INTRODUCTION

Because of their toughness, flexibility and remarkable thermal stability, linear all-aromatic polyimides are excellent candidate film and coating materials for advanced electronic circuitry and wire coating applications. In past years, however, the inherent insolubility ^(1,2) of these polymers has somewhat limited their usefulness for electronic applications.

The classic approach of incorporating aromatic pendant groups along the polymer backbone has been used successfully to improve the solubility of linear polyimides.⁽³⁻⁵⁾ Variation in the isomeric points of attachment of bridging groups in the diamine monomers has also proved effective at enhancing solubility of polyimides in common organic solvents.⁽⁶⁾ More recently, the combined effects of incorporating bulky ($-CF_3$ and $-SO_2$) groups, linking or bridging groups, and meta-linked diamines to reduce charge transfer complexing in aromatic polyimides and thereby facilitate solubility have been studied.⁽⁷⁾ Other researchers have also reported the solubility of polyimides prepared with biphenyltetracarboxylic dianhydrides in a high-boiling solvent, N-methylpyrrolidone.^(8,9)

The purpose of this investigation was to observe the effects on solubility of changing isomeric points of attachment of phenoxy units in the diamine portion of several all-aromatic polyimide systems. Hexafluoropropane- and oxygen-containing dianhydrides were used in this study because of their known value at contributing to polyimide solubility.^(6,7)

EXPERIMENTAL

Materials

The 4,4'-oxidiphthalic anhydride (ODPA) was recrystallized from anisole and sublimed at 200⁰-210⁰C/1 mm prior to use (m.p. 224⁰C). The 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) was obtained from American Hoechst and recrystallized from toluene/acetic anhydride (m.p. 241⁰C). The 4,4'-oxydianiline (4,4'-ODA) was obtained commercially, recrystallized and sublimed (m.p. 188⁰C). The 3,4'- and 3,3'-oxydianiline diamines (3,4'-ODA and 3,3'-ODA) are experimental materials obtained from Mitsui Toatsu, Inc. The 3,4'-ODA was recrystallized (m.p. 74⁰C); and the 3,3'-ODA was vacuum distilled at 125⁰C/0.1 mm (m.p. 77⁰C). Source and purity of the 2,4'-ODA has been reported ⁽¹⁰⁾ elsewhere. The 1,4-bis(4-aminophenoxy) benzene, 1,4(4)-APB; 1,3-bis(4-aminophenoxy)benzene, 1,3(4)-APB; and 1,4-bis(3-aminophenoxy)benzene, 1,4(3)-APB, were experimental diamines obtained and used as received from Mitsui Toatsu, Inc., with melting points of 171⁰, 115⁰, and 127⁰ respectively. The 1,3-bis(3-aminophenoxy)benzene, 1,3(3)-APB, was obtained commercially (m.p. 105⁰C). Dimethylacetamide (DMAc) used as a solvent for polymerization was vacuum distilled at 107⁰C over calcium hydride.

Preparation of Polymers

Polyamic acids were prepared at 15% solids (w/w) by adding the diamine and DMAc to a flask flushed with dry nitrogen. An equimolar amount of solid dianhydride was then added to the dissolved diamine. After stirring 8-24 hours at room temperature, the resulting polyamic acid solutions were refrigerated. Films were prepared by casting the amic acid resins onto soda-lime glass plates in an enclosed dust-free chamber at 10% relative humidity. Films were cured unless otherwise indicated by heating in a forced air oven for one hour each at 100⁰, 200⁰ and 300⁰C. Resulting polyimide films were approximately 1 mil (.0025 cm) in thickness.

Characterization

Melting points were determined on an E. I. DuPont Series 99 Thermal Analyzer at 20°C/min. Inherent viscosities of polyamic acid solutions were obtained at a concentration of 0.5% (w/w) in DMAc at 35°C. Glass transition temperatures (T_g) of the fully cured polymer films were measured by thermomechanical analysis (TMA) on a DuPont 943 Analyzer in air at 5°C/min. Films fully-cured at 300°C were tested for solubility at 3-5% (w/w) solids concentration in DMAc, N,N-dimethylformamide (DMF), and chloroform (CHCl_3). Solubilities at room temperature were noted after periods of 3 hours, 1 day and 5 days. Refractive indices of 1 mil thick films were obtained at ambient temperature by the Becke line method (11) using a polarizing microscope and standard immersion liquids obtained from R. P. Cargille Labs.

RESULTS AND DISCUSSION

The polyimide films prepared from the monomers shown in Figures 1-3 are listed in Table I. Reaction of monomers yielded pale yellow to colorless polyamic acid solutions with inherent viscosities ranging from 0.34 to 1.82 dl/g. Tough, flexible, transparent films were produced by thermally converting the polyamic acids to polyimides at 300°C in air. Films ranged in color from a light yellow color to essentially colorless depending on thickness. The film colors described in Table I were for nominally 1 mil thick films. Glass transition temperatures of films increased in value within each series of polymers as the linkages of the aromatic diamines were varied from all-meta to all-para. Polyimides prepared with 6F dianhydride consistently displayed higher T_g than did ODPA dianhydride-containing polymers with the same diamine. The ODPA

films had a higher refractive index ($n = 1.67-1.69$) than did the 6F polymers ($n = 1.60-1.62$). Refractive indices for these series of films was governed by the dianhydride portion of the polymer chain. These values of refractive index are all lower than the reported values of commercial polyimide film (1.78).

The solubilities of polyimide films cured at 300°C are presented in Tables II and III. Polymers prepared with ODPA dianhydride were less soluble overall in the solvents listed than those prepared with 6F. This phenomenon is not surprising as the 6F dianhydride because of its bulky $-\text{CF}_3$ groups is most effective in preventing charge transfer complexing (CTC) between polymers chains through steric hindrance.⁽⁷⁾ ODPA containing oxygen as a "separator" or "linking atom" is also effective (although less so than 6F) in producing a reduction in CTC when compared to pyromellitic (PMDA) or benzophenone tetracarboxylic (BTDA) dianhydrides. When coupled with the diamines in Figure 2, these latter two dianhydrides produce totally insoluble polymers.

The polyimides prepared with 6F dianhydride (Table II) were exceedingly soluble in the solvents studied. Solubility increased with incorporation of meta or ortho isomerism which serves to create more "kinks" and disymmetry in the polymer chains. The same trend was observed for ODPA-containing films (Table III) except to a lesser degree. Ortho isomerism appeared to have a greater effect on the solubility of ODPA films than did meta isomerism as had been noted previously.⁽⁶⁾

Several polymers were tested for solubility at high concentrations of polymer in the solvent. Previous studies had shown that ODPA + o,p'-ODA and 6F + o,p'-ODA films had a high degree of solubility in DMF at room temperature ($>40\%$ w/w).⁽⁶⁾ The polyimide powder of 6F + 3,3'-ODA was likewise tested for its solubility limit

in DMAc. The imide powder was prepared by chemically imidizing the 6F + 3,3'-ODA polyamic acid with pyridine/acetic anhydride, precipitating in distilled water, thoroughly drying at 60°C and heating for 2 hours at 200°C. This powder was gradually added to DMAc while stirring. After dissolving amounts greater than 30% (w/w) stirring became so difficult, the experiment was stopped.

Another method for solubilizing polyimide film by curing the polyamic acid for longer times at lower temperatures was attempted. The 6F + 4,4'-ODA film cured 1 hour at 300°C was found to be insoluble in DMAc at ambient temperature. The same material cured for 5 hours at 200°C was totally soluble in DMAc upon stirring for several hours. Although the T_g of this polymer was 10-15°C lower than that of the polymer cured at 300°C, the infrared spectrum of the film showed only a slight hint of anhydride -C=O peak.

CONCLUSIONS

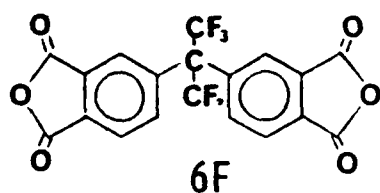
Soluble all-aromatic polyimides have been produced by coupling hexafluoropropane-(6F) and oxygen-(ODPA) containing dianhydrides with oxydianiline and bis(aminophenoxy)benzene diamines. Solubility was enhanced by the presence of meta and ortho isomer links in the diamine portion of the molecule. The polymers prepared with 3,3'-ODA and 2,4'-ODA were found to be readily soluble at > 30-40% solids at room temperature in amide solvents. These polyimides are also readily soluble in low-boiling chlorinated solvents. They can therefore be spray-coated onto desired substrates in the fully-imidized form and thus eliminate the need for taking the substrate to elevated temperatures. These soluble phenoxy-linked polyimides yield tough, flexible, colorless to pale yellow transparent films from amide or chlorinated solvents. Their potential for use in electronic applications should be excellent.

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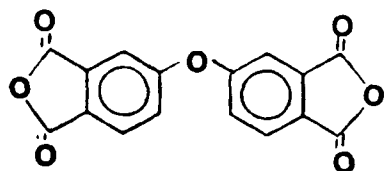
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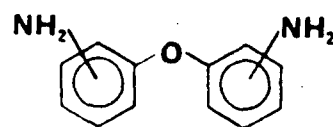


6F



ODPA

Figure 1 Dianhydride Monomers



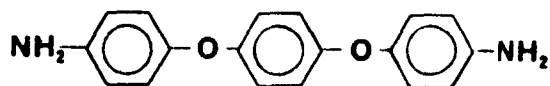
3,3'-ODA

2,4'-ODA

3,4'-ODA

4,4'-ODA

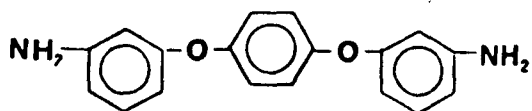
Figure 2 Oxydianiline Diamines



1,4(4)-APB



1,3(4)-APB



1,4(3)-APB



1,3(3)-APB

Figure 3 Aminophenoxybenzene Diamines

TABLE I. Properties of Polyimide Films

Polymer	n_{inh} (dl/g)	T_g , °C	Refractive Index (n)	Film Appearance
6F + 3,3'-ODA	1.00	244	1.60	Pale to Colorless
6F + 2,4'-ODA	0.75	276	--	Pale to Colorless
6F + 3,4'-ODA	0.79	280	1.60	Pale Yellow
6F + 4,4'-ODA	1.11	326	1.60	Pale Yellow
ODPA + 3,3'-ODA	1.09	186	1.69	Pale to Colorless
ODPA + 2,4'-ODA	0.77	264	1.67	Pale to Colorless
ODPA + 3,4'-ODPA	0.61	245	1.69	Pale Yellow
ODPA + 4,4'-ODA	0.34	273	1.69	Light Yellow
6F + 1,4(4)-APB	1.82	281	1.60	Light Yellow
6F + 1,3(4)-APB	1.58	255	1.62	Light Yellow
6F + 1,4(3)-APB	1.19	230	1.61	Pale to Colorless
6F + 1,3(3)-APB	1.02	209	1.61	Pale to Colorless
ODPA + 1,4(4)-APB	1.46	245	1.67	Light Yellow
ODPA + 1,3(4)-APB	1.29	217	1.69	Light Yellow
ODPA + 1,4(3)-APB	1.06	204	1.68	Pale Yellow
ODPA + 1,3(3)-APB	0.98	182	1.68	Pale to Colorless

Table II. Solubilities of Polyimide Films Prepared with 6F Dianhydride^{a,b}

Diamine	3 hr	DMAc 1d	5d	3 hr	DMF 1d	3d	CHCl ₃ 3 hr	1d	5d
3,3'-ODA	s	s	s	s	s	s	s	s	s
2,4'-ODA	s	s	s	s	s	s	s	s	s
3,4'-ODA	i	s	s	i	s	s	i	s	s
4,4'-ODA	i	i	i	i	s	s	i	s	s
1,4(4)-APB	i	i	i	i	s	s	i	s	s
1,3(4)-APB	s	s	s	s	s	s	s	s	s
1,4(3)-APB	ps	s	s	ps	ps	ps	ps	ps	ps
1,3(3)-APB	s	s	s	s	s	s	s	s	s

^aSolubilities were tested after 3 hours, 1 day and 5 days at room temperature

^bs = totally soluble; ps = partly soluble; i = insoluble

Table III. Solubilities of Polyimide Films Prepared with ODPA Dianhydride

Diamine	3 hr	DMAc 1d	5d	DMF 1d	3d	3 hr	CHCl ₃ 1d	5d
3,3'-ODA	i	s	s	i	i	s	s	s
2,3'-ODA	s	s	s	s	s	-	-	-
3,4'-ODA	i	i	i	i	i	i	i	i
4,4'-ODA		i	i	i	i	i	i	i
1,4(4)-APB	i	i	i	i	i	i	i	i
1,3(4)-APB	i	i	i	i	i	i	i	i
1,4(3)-APB	i	i	i	i	i	i	i	i
1,3(3)-APB	ps	ps	ps	ps	ps	ps	ps	ps

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16. Abstract Linear all-aromatic polyimides have been synthesized and characterized which show much potential as films and coatings for electronic applications. Structure-property relations with regard to methods for obtaining solubility of fully imidized polymers will be discussed. Methods used to obtain solubility include variation of polymer molecular structure, variation of isomerism of the diamine monomer, modification of cure time/temperature and atmosphere. Other properties of soluble polyimides will be presented which include glass transition temperatures, thermooxidative stabilities, UV-visible spectra, and refractive indices.					
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